

DEVELOPMENT OF MERCURY CONTROL TECHNOLOGY FOR COAL-FIRED SYSTEMS

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INTRODUCTION

The emission of hazardous air pollutants (air toxics) from various industrial processes has emerged as a major environmental issue that was singled out for particular attention in the Clean Air Act Amendments of 1990. In particular, mercury emissions are the subject of several current EPA studies because of concerns over possible serious effects on human health. Some of those emissions originate in the combustion of coal, which contains trace amounts of mercury, and are likely to be the subject of control requirements in the relatively near future. Data collected by the Department of Energy (DOE) and the Electric Power Research Institute (EPRI) at operating electric-power plants have shown that conventional flue-gas cleanup (FGC) technologies are not very effective in controlling emissions of mercury in general, and are particularly poor at controlling emissions of elemental mercury. This paper gives an overview of research being conducted at Argonne National Laboratory on improving the capture of mercury in flue gas through the use of dry sorbents and/or wet scrubbers.

BACKGROUND

Mercury emissions from coal combustion have been shown to vary considerably from site to site. Those emissions depend not only on the composition of the coal, but also upon the type of boiler, the operating conditions, and the FGC system. Mercury belongs to a group of elements/compounds denoted as Class III, which remain primarily in the vapor phase within the boiler and subsequent FGC system. However, that state can be influenced by reactions with other elements, such as chlorine, and by fly-ash characteristics that affect adsorption processes. The concentration of mercury in the flue gas from typical coal combustors ranges from less than 10 to more than 50 $\mu\text{g}/\text{Nm}^3$.

Few reliable data on mercury control have been available for FGC technologies used on coal-fired systems. Large variations in reported removals have been typical, due both to differences in coal and operating characteristics and to inaccuracies in sampling/analytical procedures.¹ Particulate-matter collectors, such as electrostatic precipitators (ESPs) and baghouses, can be effective for mercury control to the extent that mercury is adsorbed on the fine particulate matter (fly ash) in the gas stream or is converted to another chemical form that can be collected as particulate matter. Recent data on mercury removals for ESPs range from about 15 to 75%, while very limited removal data for baghouses range from 10 up to 70%. Mercury removal in wet flue-gas desulfurization (FGD) systems is also quite variable, with values ranging from near zero to about 50%.² Much of that variation may be caused by differences in the chemical form of the mercury, inasmuch as the chloride is much more easily captured than the elemental form. Most available information on mercury control technologies for combustion sources has originated in work with waste incinerators. In such cases, activated carbon has been shown to be an effective sorbent for mercury. However, flue-gas conditions at incinerators are much different in temperature and composition than those found at coal-fired utility boilers, and the performance/economics of activated carbon can be expected to vary as well. In addition, the presence of wet FGD systems at many utility boilers presents a considerably different set of conditions and problems/opportunities that need to be evaluated.

RESEARCH PROGRAM

Based on an initial survey of published information, a number of chemical additives and sorbents with the potential for enhancing the capture of elemental mercury in dry or wet/dry FGC systems were selected for laboratory investigation. The study of dry sorbents was chosen for several reasons. Many existing coal-fired plants have only particulate-matter control, usually in the form of ESPs, and these could be well suited to duct- or furnace-injection of mercury sorbents. Also, European experience with the addition of sorbents/chemicals to spray-dryer systems on municipal waste incinerators has indicated that greatly enhanced mercury removals are possible. A more extensive discussion of this research can be found in Reference 3. The research program also includes investigation of mercury removal in wet scrubbing. The initial study found very little information regarding potential performance enhancements for scrubbers operating on coal-fired systems, although some work has been done for applications in other industries.⁴ To date, the research has focused on physical modifications designed to improve the absorption of mercury

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by the scrubber liquid, on the testing of chemical agents selected for their potential to react with mercury, and on process modifications designed to combine gas-phase and liquid-phase reactions.

EXPERIMENTAL FACILITIES

Argonne's FGC-laboratory facilities include a fixed-bed reactor system for studying dry sorbents, a complete wet scrubber system, and a spray-dryer/fabric-filter system. Supporting facilities include a system that can provide known concentrations of elemental mercury in a gas stream, a gas-supply system capable of blending synthetic flue gas from bottled gases, on-line gas-analysis packages, and data loggers. The following sections briefly describe the key systems. More detailed descriptions of all of the systems can be found in References 5 and 6.

Mercury Supply and Analysis

The feed-gas preparation system consists of a mercury-containing permeation tube, a constant-temperature water bath, and a carrier-gas supply. The design capacity of the system is 20 L/min of gas with mercury concentrations of up to 100 $\mu\text{g}/\text{m}^3$. Mercury measurements are made using a gold-film mercury-vapor analyzer. The range of the instrument is 0 to 999 $\mu\text{g}/\text{m}^3$ with a sensitivity of 3 $\mu\text{g}/\text{m}^3$ and an accuracy of $\pm 5\%$ at 100 $\mu\text{g}/\text{m}^3$.

Fixed-Bed Reactor

The fixed-bed reactor vessel, which is constructed of glass, is 4 cm in diameter and 14 cm in height. A glass frit is positioned in the lower section to support materials placed inside the reactor. To avoid fluidization of the bed materials, the feed gas enters the reactor from the top and exits at the bottom. During shakedown and baseline tests, the reactor was packed with either silica sand (120 g) or a mixture of silica sand and hydrated lime ($\text{Ca}(\text{OH})_2$) in a weight ratio of 40:1. The $\text{Ca}(\text{OH})_2$ has been employed because it is a common sorbent for SO_2 in FGC systems. The large amount of sand is used to avoid channeling caused by lime agglomeration. For additive/sorbent testing, small amounts of material being studied are added to the sand/ $\text{Ca}(\text{OH})_2$ bed material. To maintain a uniform temperature during experiments, the reactor is immersed in a fluidized-bed, constant-temperature sand bath. To preheat the incoming feed gas to a temperature equal to that maintained in the fixed-bed reactor, the gas-transfer line is wrapped with heating tapes.

Wet Scrubber

All of the principal vessels in the wet-scrubber system are constructed of glass. The scrubber column has an inside diameter of 7.6 cm and an active height of nearly 53 cm. It is normally operated in a countercurrent mode with the flue gas entering at the bottom. The scrubber is constructed of several interchangeable sections so that it can be configured as a flooded column (no internals), a four-stage disc and donut column, or an intermediate combination. For most of the experiments described here, the combination mode was used with the lower part of the column left open to accommodate packing. The scrubber liquor drains into a holding tank from which it is recirculated to the top of the scrubber. The temperature of the liquor can be adjusted by heating the holding tank with heat tapes. The pH of the liquid in the tank is sampled continuously and can be adjusted either manually or automatically by adding reagent from a chemical feed tank.

EXPERIMENTAL RESULTS

Experiments with Dry Sorbents/Additives

Following initial shakedown tests that verified that neither the sand nor the lime in the fixed bed gave any measurable mercury removal, a variety of dry sorbents were studied. Various sorbents and chemical additives for mercury removal have been reported in the literature. These include activated carbon, activated carbon impregnated with various chemicals (notably sulfur and iodine), modified zeolites, glass fibers coated with special chemicals, and pure chemicals (such as sulfur, selenium, and ferrous sulfide and sulfate). In addition to comparing the performance of different types of sorbents/additives, the research program has included investigation of the effects of varying process parameters, such as sorbent particle size, sorbent loading in the reactor, reactor/gas temperature, and mercury concentration.³ For most of the tests, the amounts of sorbent added ranged from 1 to 10 wt% (relative to the lime). Three fixed-bed reactor temperatures were evaluated: 55, 70, and 90°C. Target mercury concentrations in the nitrogen feed gas of either 44 or 96 $\mu\text{g}/\text{m}^3$ were used, and the feed-gas flow rate was fixed at 10 L/min.

By far the best removal results in the initial tests were obtained with an activated carbon that was commercially treated with about 15 wt% sulfur. The success of the sulfur-treated carbon is thought to be based on a combination of physical adsorption and chemical reactions that produce mercury sulfide. This suggests that chemical additives producing other compounds, such as mercury chloride, might also be beneficial for removals. To explore this possibility, another carbon sample that previously gave essentially no removal was treated with calcium chloride (CaCl_2) in the ratio of about 6:1 by weight. The treated carbon gave excellent removals and actually performed better than the sulfur-treated carbon.

Recently, the research has been focused on the development and testing of lower-cost alternatives to activated carbon. Several high-surface-area or low-cost mineral substrates have been identified and samples have been obtained. Tests of the materials in the as-received condition gave moderate mercury removals for a molecular sieve sorbent and essentially no removals for pumice and vermiculite samples. In current research, the samples are being treated with chemical additives shown to be effective with activated carbon and tests are being run at various additive concentrations, mercury concentrations, and flue-gas temperatures. Figure 1 gives the results of experiments with volcanic pumice treated with

potassium iodide, CaCl_2 , or sulfur. The untreated pumice was ineffective for mercury removal, but the sulfur-treated sorbent gave 100% removal for over an hour, while the iodide-impregnated sorbent gave 100% removal for a few minutes followed by a decrease in removal that appeared to level out at about 30%. In order to explore the effects of temperature on the treated sorbents, additional tests were run at a temperature of 150°C. As shown in Figure 2, the iodide-impregnated sample behaved very similarly at the two temperatures. However, the sulfur treatment that was so effective at the lower temperature was found to be totally ineffective at the higher temperature. This may be due to a change in the form of the sulfur, but this issue is still under study and has not yet been resolved.

Experiments with Wet Scrubbing

Preliminary data from field-sampling campaigns have indicated that elemental mercury is not appreciably removed in typical wet-scrubber systems. This is not surprising given the very low solubility of mercury in the elemental form. Initial experiments were conducted using the scrubber as described above, no packing, and various degrees of "flooding" in the lower part of the column to promote gas-liquid contact. The scrubbing liquors tested were distilled water, a saturated Ca(OH)_2 solution, and a Ca(OH)_2 solution with 1000 ppm of potassium polysulfide. The polysulfide has been claimed to promote mercury removal in other research.⁴ The mercury inlet concentration was about 40 $\mu\text{g}/\text{m}^3$, the liquid height in the column was varied up to 43 cm, and the temperature was varied between 22 and 50°C. No mercury removal was detected under any of these conditions.

The addition of ceramic-saddle packing to the column produced removals of 3 to 5% with distilled water at 22°C, and removals of 6 to 7% were obtained when the temperature was raised to 55°C. However, tests involving polysulfide addition had to be terminated when reactions with the ceramic saddles produced hydrogen sulfide (H_2S) that interfered with the operation of the mercury analyzer.

In earlier research on mercury capture, stainless steel packing was found to promote mercury capture.⁴ Therefore, the ceramic saddles were replaced by 0.61-cm stainless-steel packing, which gave the rather unexpected result of 11% removal with no liquid in the column. Removals with water in the column ranged from 15 to 20%. Addition of polysulfide to the scrubber produced a noticeable increase in removal up to about 40%. It appears that there is a positive synergistic effect on removal involving the combination of polysulfide and stainless steel. It should be noted that this additive requires a very high pH to maintain its stability and this may preclude its use in most FGD systems.

In an effort to promote greater mercury capture through changing its chemical form, tests were conducted with several additives that combine strong oxidizing properties with relatively high vapor pressures. Tests with minimal gas-liquid contacting yielded mercury removals as high as 100%, and indicated that the removal reactions were occurring in the gas phase above the scrubber liquor. However, tests with the addition of SO_2 to the gas stream showed the additives to be very reactive with that species as well, which could result in excessively high additive consumption in order to realize effective mercury control. Recently, tests with a new combination of oxidizing chemicals, NOXSORB™, which is a product of the Olin Corporation, have indicated promise for integrated removal of several flue-gas species including mercury. Preliminary data from those tests are shown in Figure 3. Further tests are exploring the effects of different additive concentrations, the relationship between NO/SO_2 removal and mercury removal, and possible process configurations and economics.

CONCLUSIONS

The results and conclusions to date from the Argonne research on dry sorbents can be summarized as follows:

- Lime hydrates, either regular or high-surface-area, are not effective in removing elemental mercury.
- Mercury removals are enhanced by the addition of activated carbon.
- Mercury removals with activated carbon decrease with increasing temperature, larger particle size, and decreasing mercury concentration in the gas.
- Chemical pretreatment (e.g., with sulfur or CaCl_2) can greatly increase the removal capacity of activated carbon.
- Chemically treated mineral substrates have the potential to be developed into effective and economical mercury sorbents.
- Sorbents treated with different chemicals respond in significantly different ways to changes in flue-gas temperature.

Preliminary results from the wet scrubbing research include:

- No removal of elemental mercury is obtained under normal scrubber operating conditions.
- Mercury removal is improved by the addition of packing or other techniques to increase the gas-liquid contact area.

- Stainless steel packing appears to have beneficial properties for mercury removal and should be investigated further. Beneficial synergisms with polysulfide solutions have been observed.
- Oxidizing additives may be used in conjunction with wet scrubbing to greatly enhance removals. Selectivity is required to avoid excessive additive consumption from competing reactions.

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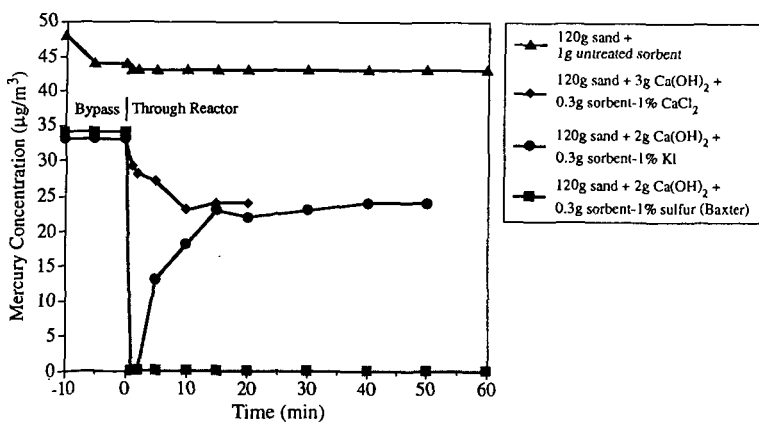


Figure 1. Effects of chemical pretreatment on an inert substrate at 70°C.

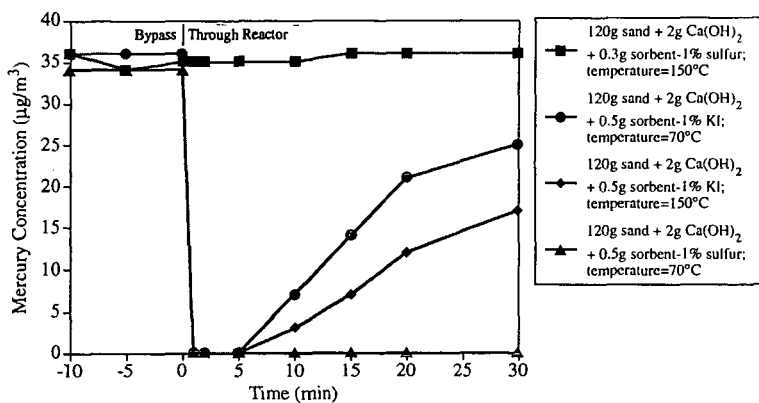


Figure 2. Effects of different temperatures on a chemically pretreated inert substrate.

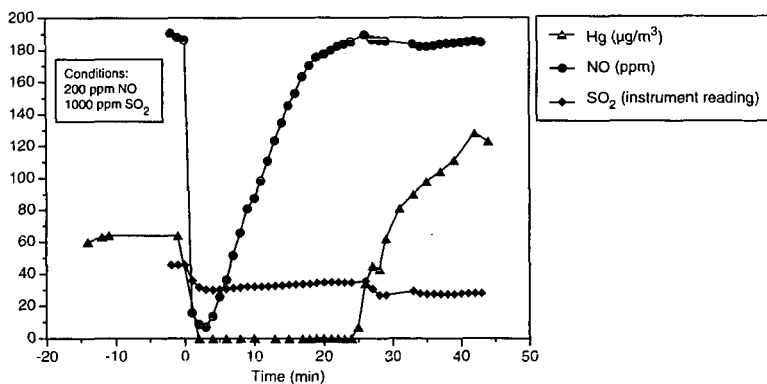


Figure 3. Removals of Hg, NO, and SO_2 in the wet scrubber with a 4% NOXSORB™ solution.